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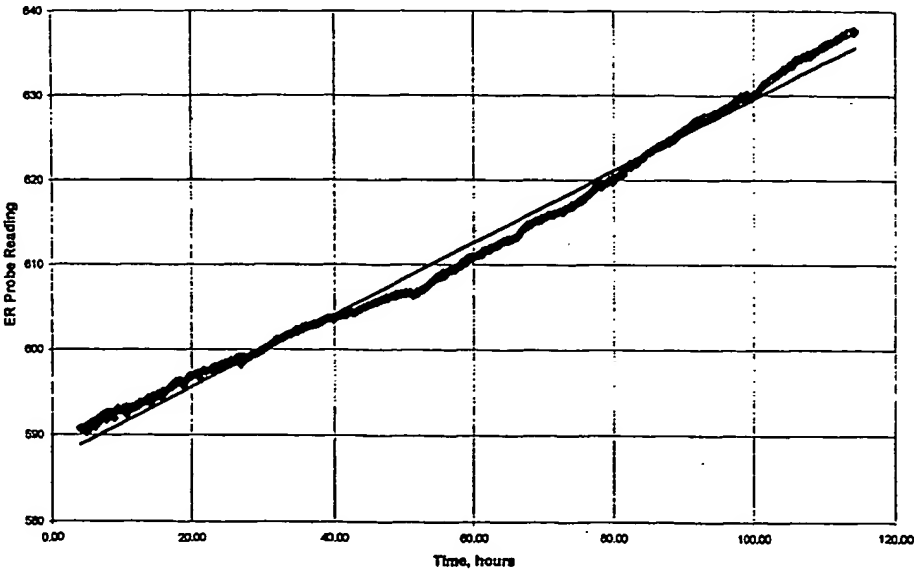
(54) Title: METHODS FOR INHIBITING HIGH TEMPERATURE CORROSION



(57) Abstract

The present invention provides for methods for forming a durable, corrosion–inhibiting film on the surface of metals in crued oil processing systems by the periodic addition of a film forming phosphorus–containing compound. This periodic addition will inhibit corrosion without the costly need for continuous maintenance dosages.

METHODS FOR INHIBITING HIGH TEMPERATURE CORROSION

FIELD OF THE INVENTION

The present invention relates to methods for inhibiting corrosion of process equipment in high temperature crude oil processing. More particularly, the present invention relates to the periodic addition of a film forming phosphorous-containing compound to the crude oil, crude oil fractions and residua to provide for a tenacious durable film on the surfaces of the processing equipment without the need for continuous maintenance dosages.

BACKGROUND OF THE INVENTION

Hydrocarbon and petroleum refining operations suffer corrosion problems due in part to naphthenic acid constituents and sulfur compounds in crude oils. This corrosion is particularly severe in atmospheric and vacuum distillation units operating at temperatures between about 400° and 790°F. The amount of naphthenic acid constituents and sulfur compounds, the velocity and turbulence of the

The present inventors have demonstrated through use of the present invention that inhibitor usage and cost are reduced by as much as 80% over continuous treatment addition.

DESCRIPTION OF THE RELATED ART

U.S. Pat. No. 4,941,994 teaches methods for inhibiting metal corrosion in hot acidic liquid hydrocarbons comprising adding to the hydrocarbons a dialkyl and/or trialkyl phosphite compound and, optionally, a thiazoline compound. The '994 patent notes that a high initial dosage of inhibitor is preferred for a short time to build up a protective coating on the metal surfaces. Once the protective surface is established, the dosage rate may be lowered to maintain the protective surface.

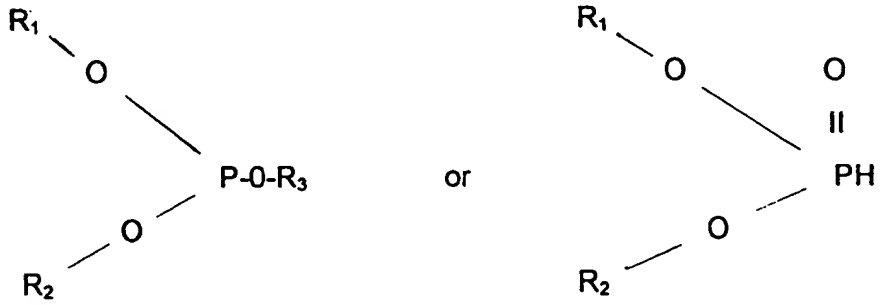
U.S. Pat. No. 5,500,107 teaches methods for inhibiting the corrosion of the metal surfaces of equipment used in processing crude oil comprising adding to the crude oil of a phosphite compound containing at least one aryl group. This patent also states that it is preferred to add a high initial dosage rate and to maintain this level for a very short time. This induces a build-up of a protective coating which, once established, can be maintained with a lower rate of addition.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph of corrosion rate versus time for 1010CS (Carbon Steel) at 600°F in heavy vacuum gas oil (HVGO) without an inhibitor added.

Representative phosphorus-containing compounds include but are not limited to trialkyl phosphates having an alkyl moiety of C_1 to C_{12}. Preferred trialkyl phosphates are selected from the group consisting of trimethyl phosphate, triethyl phosphate, tripropyl phosphate, tributyl phosphate (TBP) and tripentyl phosphate.

Other representative phosphate-containing compounds include phosphite compounds containing at least one aryl group represented by the formulas:



wherein R_1, R_2 and R_3 are C_6 to C_{12} aryl or alkyl and at least one R group is aryl.

Exemplary aryl containing phosphites include triphenyl phosphite, diphenyl phosphite, diphenyl isodecyl phosphite, diphenyl isooctyl phosphite, and phenyl diisodecyl phosphite (PDDP). These compounds are commercially available from GE Specialty Chemicals Company.

Other phosphorus-containing compounds include phosphate ester compounds such as mono- and di-(2-ethylhexyl) phosphate esters and mixtures thereof which are available from Chemax, Inc. as Chemfac PA-080.

This amount will vary with local operating conditions and the particular hydrocarbon being processed. Temperature and amounts of naphthenic acids and sulfur compounds will also affect the amount of phosphorus-containing compounds added. Typical processing temperatures range from about 350° to 1000°F with a range of 400° to 790°F more preferred.

The long lasting and durable nature of the film formed will allow for the addition of the film forming phosphorous-containing compounds on a periodic basis. One measure of time between additions may be based on when the film formed begins to lose effectiveness. This interval will also be dictated by the above-varied operating conditions and by economy of usage.

For purposes of the present invention, durable may be defined as the length of time that is measured in terms of hours to days rather than in seconds to minutes.

For purposes of the present invention, crude oils comprise crude oil and its fractions or residua produced or left after normal refinery processing steps, such as desalting, distillation, cracking, coking, extraction, hydrogenation, isomerization, or alkylation.

The invention will now be further described with reference to the following examples which are intended for illustration purposes and should not be construed as limiting the invention.

Table I (Continued)

Example No.	Treatment (ppm)	Corrosion Rate (mpy)		Approximate Time (Hours)
4	0	5.6	Precorrosion	23
	100	1.4	Before Fluid Change	23
	0	0.1	After Fluid Change Film Persistency Step	76
	0	2.3	Film Failure Step	23
5	0	7.0	Precorrosion	23
	200	1.0	Before Fluid Change	23
	0	1.2	After Fluid Change Film Persistency Step	92
	0	7.4	Film Failure Step	20

As demonstrated by Figures 1 to 5 and the results of Table I, the use of a phosphorus-containing compound proved effective at providing a durable, long lasting film on the 1010 CS metal. Example 1 and Figure 1 show the corrosion behavior of uninhibited Heavy Vacuum Gas Oil from a southern refinery, which is fairly constant over a five-day period.

Example 2 and Figure 2 demonstrate the effects of fluid change after 24 hours where the uninhibited fluid was removed by N_2 pressure. Corrosion rates between the two were essentially the same.

In Example 3 and Figure 3, 100 ppm of Chemfac PA-080 was injected into the HVGO shortly after the test temperature was attained. The inhibitor was allowed to film the probe for about 25 hours. At that time, the treated fluid was replaced with fresh, untreated fluid. As shown in Figure 3, excellent corrosion inhibition was observed both when the inhibitor was present in the fluid and after the fluid change when no inhibitor was added to the fluid.

Table II

Two Step Weight Loss Method
Pretreatment Data - High Acid Gas Oil

Inhibitor	Dosage (ppm) Pretreatment/ Maintenance	Maintenance Corrosion Rate (mpy)
Low Acid Gas Oil Blank	-/0	5.9
High Acid Gas Oil Blank	-/0	14.1
High Acid Gas Oil Control	0/0	5.4
PDDP	200/0	2.4
PDDP	400/0	1.4
PDDP	400/100	1.0
TBP/E-686	400/0	0.3
TBP/E-686	400/100	1.0
TBP	62/0	1.2
TMT-3H	100/0	8.4

PDDP is phenyl diisodecyl phosphite.

TBP is tributyl phosphate.

E-686 is a calcium overbased phosphonate phenate sulfide, available from Ethyl Corp. as HITEC E686.

TMT-3H is 2, 4, 6-trimercapto- 1, 3, 5-triazine, available from Degussa.

As demonstrated in Table II, the untreated, low acid blend gave a corrosion rate of 5.9 mpy. When coupons exposed to the untreated, low acid blend were subsequently exposed to the high acid gas oil, the calculated high acid gas oil corrosion rate was 5.4 mpy. Comparing this value to the value of 14.1 mpy measured in the high acid gas oil using unexposed coupons indicates that the sulfide film formed during the low acid blend exposure provide significant protection against corrosion.

much as 80% by eliminating the maintenance dosage. In Table II, the films formed were able to last for about 24 hours at a minimum without maintenance dosages.

While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of this invention will be obvious to those skilled in the art. The appended claims and this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the present invention.

3. The method as claimed in claim 2 wherein said trialkyl phosphate is selected form the group consisting of trimethyl phosphate, triethyl phosphate, tripropyl phosphate, tributyl phosphate, and tripentyl phosphate.

4. The method as claimed in claim 2 wherein said aryl containing phosphite is selected from the group consisting of triphenyl phosphite, diphenyl phosphite, diphenyl isodecyl phosphate, diphenyl isooctyl phosphite, and phenyl diisodecyl phosphite.

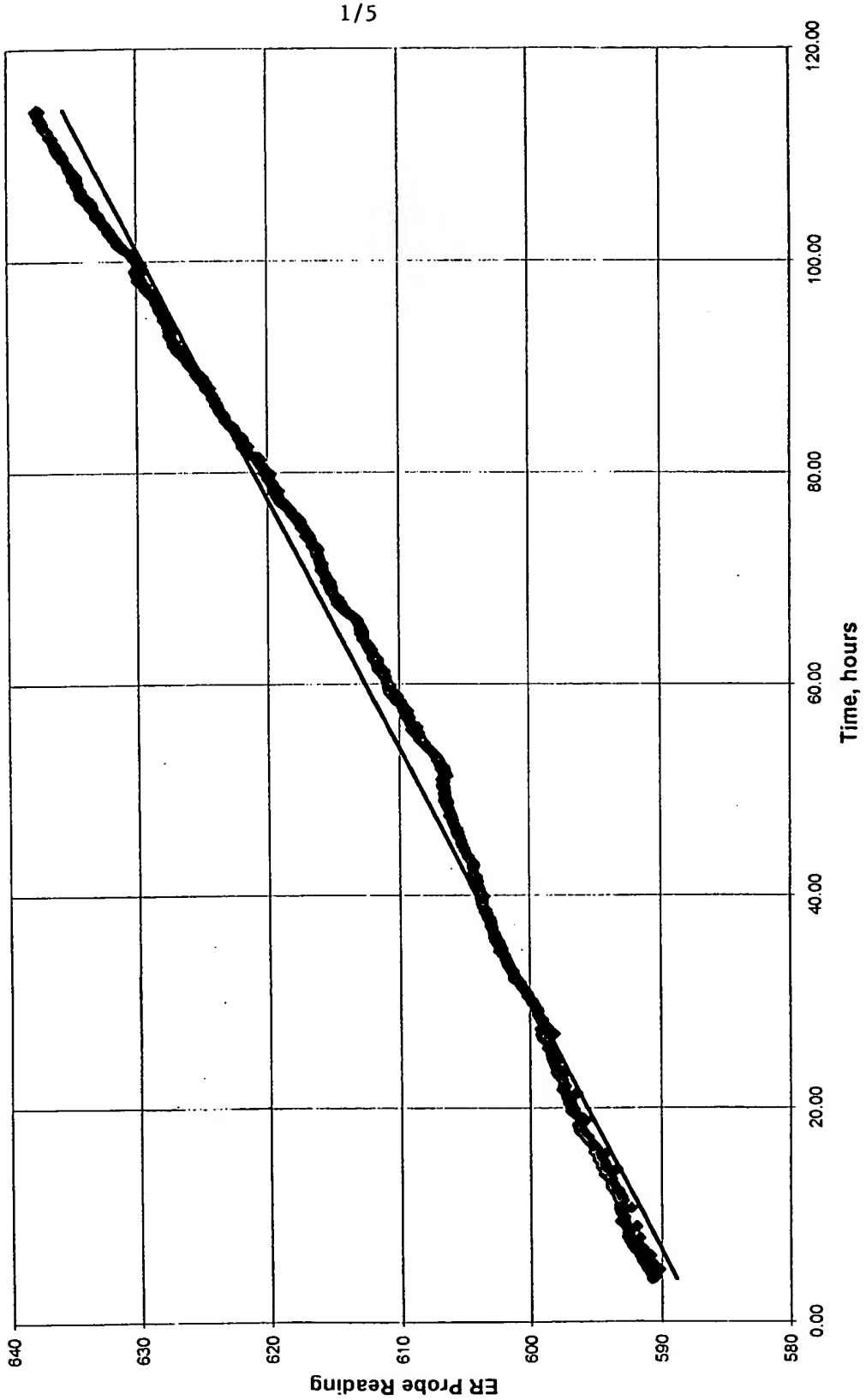
5. The method as claimed in claim 2 wherein said phosphate ester compound is selected from the group consisting of mono- and di-(2-ethylhexyl) phosphate esters and mixtures thereof.

6. The method as claimed in claim 1 wherein said effective amount ranges from about 10 parts to about 10,000 parts per million parts of crude.

7. The method as claimed in claim 2 wherein said alkyl phosphonate phenate sulfide is a calcium overbased phosphonate phenate sulfide.

8. The method as claimed in claim 1 wherein said crude oil processing system is an atmospheric or vacuum distillation unit.

9. The method as claimed in claim 1 wherein said crude oil comprises crude oil, its fractions and residua.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80.00
60.00
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20.00
0.00
Time, hours
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630
620
610
600
590
580
ER Probe Reading

FIGURE 1

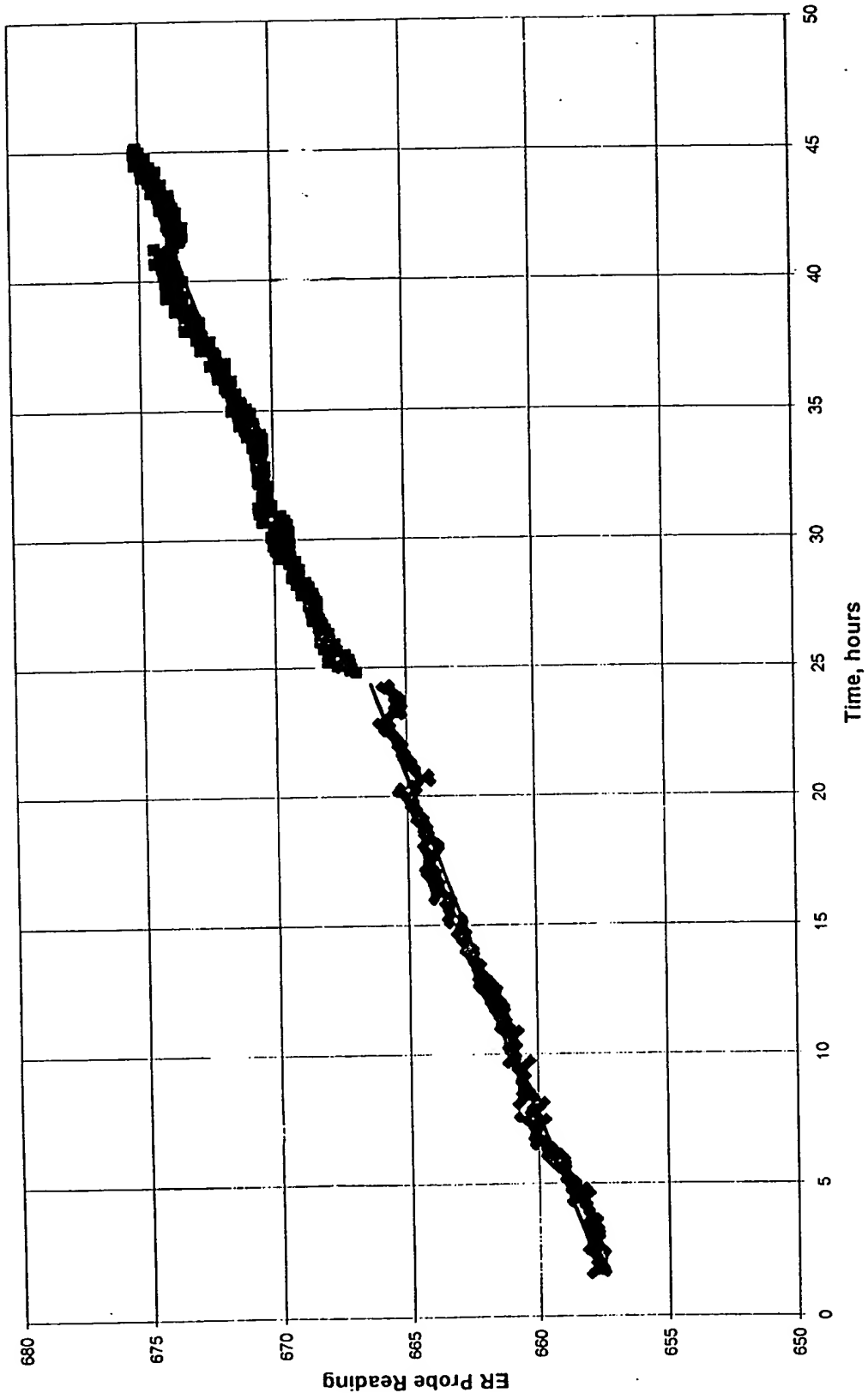
ER Probe Reading
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FIGURE 2

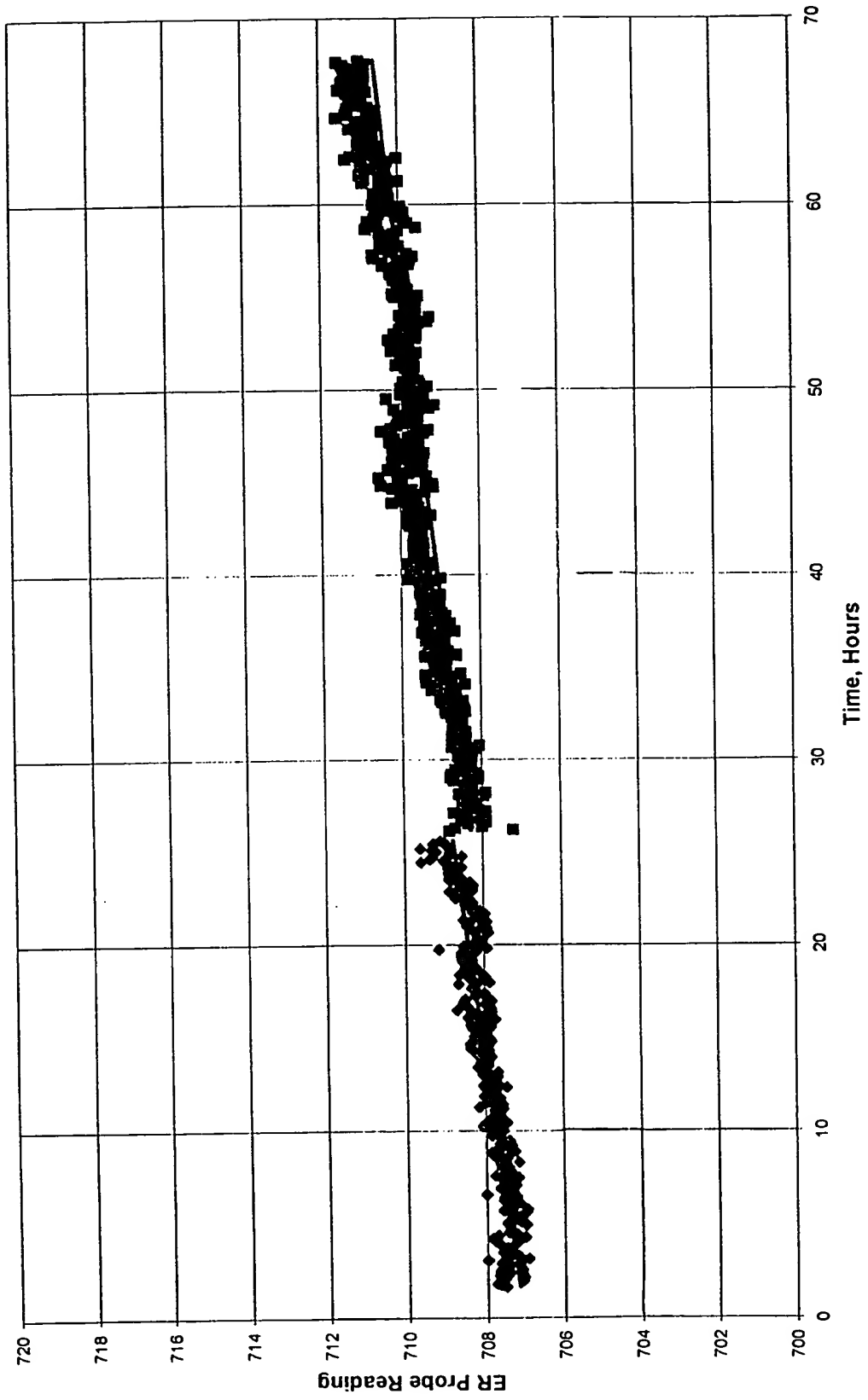
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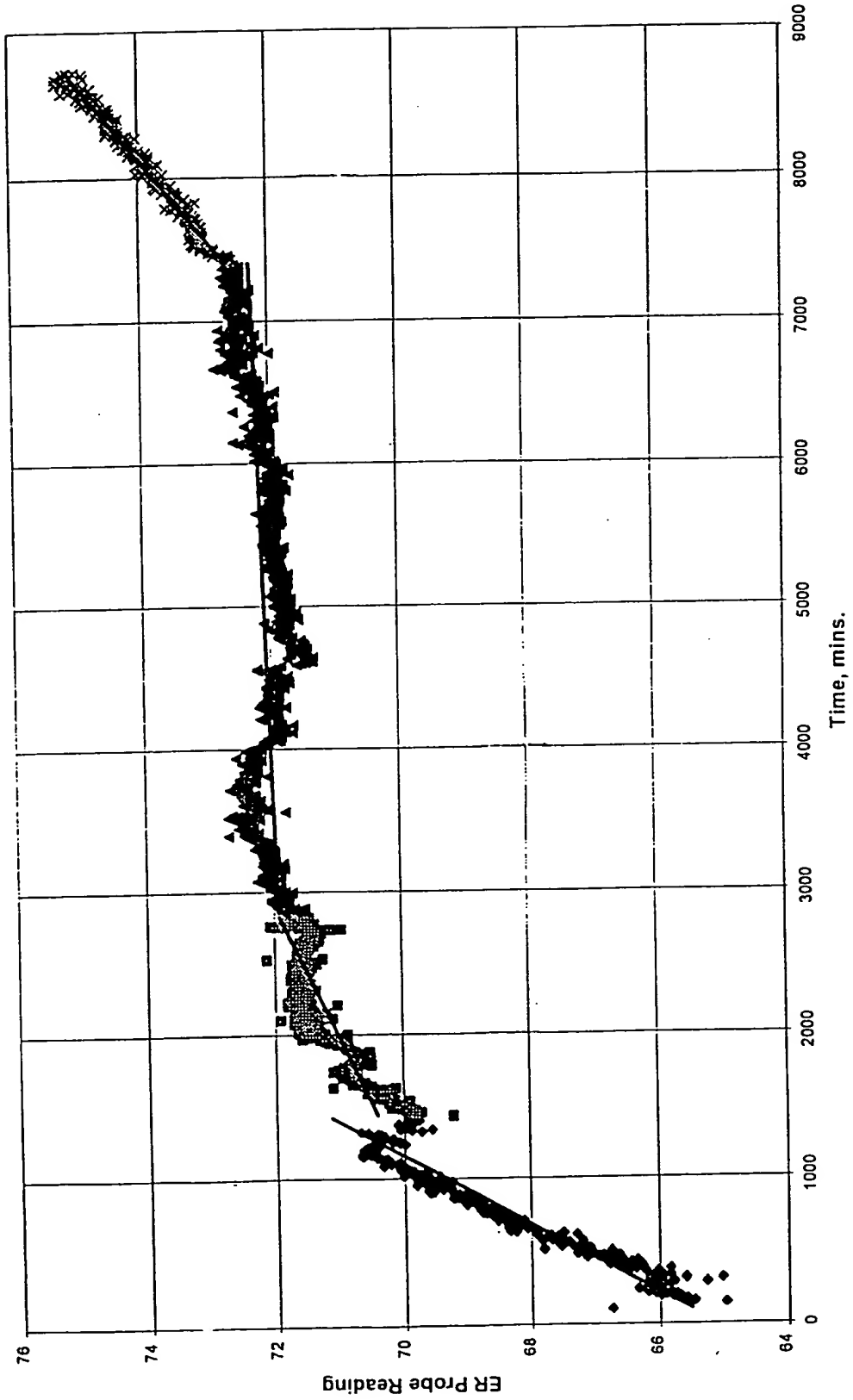
FIGURE 3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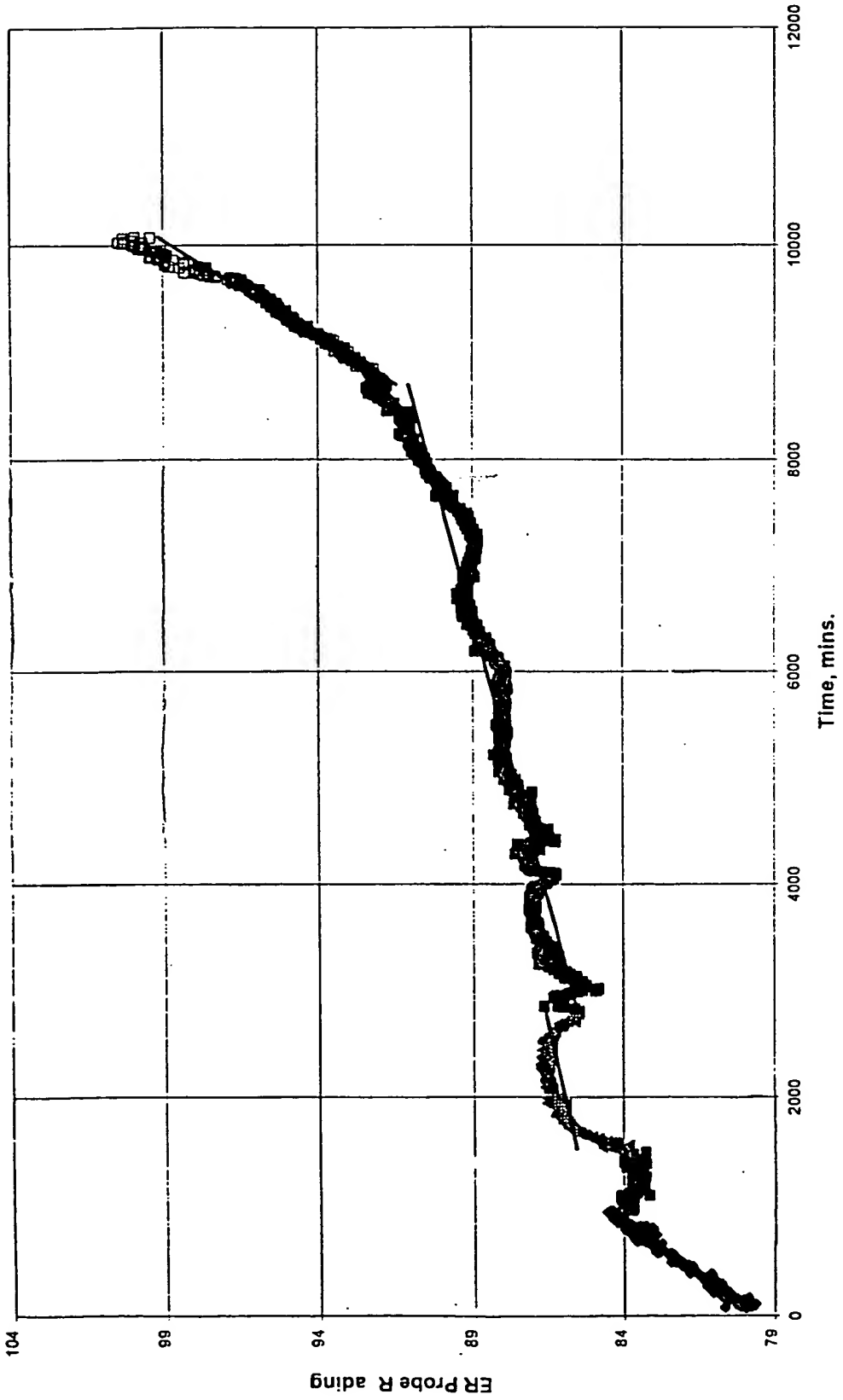
9000

FIGURE 4


ER Probe R ading
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Time, mins.
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2000
4000
6000
8000
10000
12000

FIGURE 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/18917

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C10G 9/12
US CL : 208/47, 48R, 48AA; 585/950

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/47, 48R, 48AA; 585/950

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS:
search terms: corrosion, napththenic acid? phosphorus?

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,500,107 A (EDMONDSON) 19 March 1996 (19-03-96), claims, column 3, lines 6-10	1-9
X	US 4,927,519 A (FORESTER) 22 March 1990 (22-03-90), column 1, lines 20-25; column 2, lines 60-65; column 4, lines 27-54; column 5, lines 5-55; column 7, lines 20-35; column 9, lines 30-40; column 11, lines 12-22.	1-9

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 07 DECEMBER 1997	Date of mailing of the international search report 30 JAN 1998
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer BEKIR L. YILDIRIM Telephone No. (703) 308-0661

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